

# PATENT SPECIFICATION

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805.861



Date of filing Complete Specification May 28, 1957.

Application Date May 31, 1956.

No. 16871/56.

(Patent of Addition to No. 784,638 dated Sept. 21, 1955).

Complete Specification Published Dec. 17, 1958.

Index at acceptance:—Classes 1(1), A3B1; and 2(3), C3A13A1(A1:K), C3A13A3(A1D:B1:K).

International Classification:—B01j, C07c.

## COMPLETE SPECIFICATION

### Catalysts

We, THE BRITISH OXYGEN COMPANY LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to catalysts and more particularly to copper acetylide catalysts for the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, and is an improvement in or modification of the invention described and claimed in our co-pending Application No. 27318/54 (Serial No. 784,638).

2-butyne-1:4-diol (hereinafter referred to as butynediol) is usually prepared by reacting acetylene with an aqueous solution of formaldehyde in the presence of a catalyst consisting essentially of copper acetylide. The catalyst can be prepared by reacting an aqueous solution of a copper salt with acetylene under appropriate conditions, removing the precipitated copper acetylide and transferring it to the vessel in which the acetylene and the formaldehyde are to be reacted. This procedure may give rise to difficulties in handling the free copper acetylide (which can decompose explosively when dry) and, moreover, it has been found that the catalyst particles are liable to attrition during the course of reaction, so that difficulties arise in separating the catalyst and the product liquor.

To obtain a more robust catalyst, it has been proposed to support the catalyst on a porous solid medium, the procedure being to deposit the copper salt on the support and to convert it to copper acetylide *in situ*. A preferred support has been silica gel, and in order to obtain a satisfactory catalyst, it has been necessary for the catalyst support to be specially prepared. Catalysts have been described in which the amount of copper held on the support was 10—12% by weight.

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In Application No. 27318/54 (Serial No. 784,638), there is claimed a process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol comprising as a first stage, preparing a copper silicate material containing 15—60% by weight of copper by mixing the requisite proportions of a solution of a copper salt and a solution of an alkali metal silicate, and subsequently treating the copper silicate material with acetylene to convert the copper content of the material to copper acetylide.

It is an object of the present invention to provide a catalyst which is still more efficient than that described in Application No. 27318/54 (Serial No. 784,638).

According to one aspect of the present invention, the process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol described and claimed in Application No. 27318/54 (Serial No. 784,638) is modified by replacing a part of the solution of sodium silicate by a solution of sodium hydroxide, potassium hydroxide, or ammonium hydroxide.

According to another aspect of the present invention, a process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, comprises as a first stage the preparation of a basic copper silicate material containing 15—60% by weight of copper by mixing the requisite proportions of a copper salt, a solution of an alkali metal silicate, and a solution of sodium hydroxide, potassium hydroxide, or ammonium hydroxide, and subsequently treating the thus formed basic copper silicate material with acetylene to convert the copper content of the material to copper acetylide.

The basic copper silicate precipitate may be separated, washed, and dried by heating in air to temperatures up to 500° C. or above, or

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by warming to only slightly elevated temperature under reduced pressure. When drying at atmospheric pressure the preferred upper temperature limit is 300° C. The dried material forms cakes which can be readily reduced in size to any required shape or form, for example, the material may be extruded into rods or converted into other suitable forms. It can, if desired, be mixed with inert materials such as kaolin, and then pelleted. If the material is heated above about 100° C. in the drying process, its colour may change from light blue to black, but catalysts can be prepared from either the blue or the black material.

It is possible, if desired, to impregnate the copper silicate material with further amounts of copper by immersion in a solution of a copper salt and subsequent ignition. In this way, the copper content of the final material can be raised to 60% or more, but this is not essential for the preparation of a useful catalyst.

It is possible to convert the precipitated copper silicate into a copper acetylide catalyst without prior separation from its mother liquor, but this is not a preferred method of operating the process of our invention.

It is sometimes considered desirable to incorporate in the catalyst for the reaction between acetylene and formaldehyde other materials generally described as "cuprene inhibitors". A particularly useful example of such inhibitors is bismuth.

The basic copper silicate catalyst prepared and used in accordance with the method described in this patent application does not require the addition of cuprene inhibitors mentioned above as it has been found that cuprene formation is almost negligible when the new method of preparation of the catalyst is used.

The copper silicate material may be converted into the actual catalyst used in the reaction by adding it to aqueous formaldehyde which is warmed above 60° C. and feeding acetylene to it. The conversion may conveniently be carried out *in situ* in the reactor. The catalyst so prepared is robust. In batch processes in which the catalyst is suspended in aqueous formaldehyde and the latter reacted with acetylene under pressure, the product liquor subsequently being separated from the catalyst which is then re-used, the catalysts of the present invention can be used repeatedly for a large number of successive operations. The separation of product liquor and catalyst remain facile even after much repeated use of the same batch of catalyst. In continuous operation in which aqueous formaldehyde and acetylene are each flowed through a bed of catalyst, catalysts prepared according to the present invention are much less subject to attrition, to dislodgement of copper acetylide, or to blockages causing resistance to flow than

are either unsupported copper acetylide or copper acetylide supported on preprepared supports.

It is a further advantage of catalysts prepared in accordance with the present invention that a given amount of such a catalyst is capable of catalysing the reaction between acetylene and formaldehyde to a greater extent than the same amount of the catalysts which was the subject of Application No. 27318/54 (Serial No. 784,638).

A preferred method of carrying out the reaction between acetylene and formaldehyde using the catalyst of the present invention comprises suspending the catalyst in formaldehyde solution and maintaining it in suspension by passing through the solution acetylene or an acetylene containing gas under super-atmospheric pressure, the product being subsequently separated from the catalyst by filtration or centrifugation. As mentioned above, cuprene formation is almost negligible when using the catalyst of the present invention and is insufficient to interfere with the rapid filtration of the reaction product. The catalyst bed is readily re-suspended in a fresh charge of aqueous formaldehyde and the process can be repeated many times.

It is a further advantage of the process operated in this manner that the acetylene or acetylene inert gas mixtures leaving the reaction zone carries with it substantial quantities of water vapour, propargyl alcohol and some formaldehyde, removing thereby a substantial proportion of the heat liberated during the reaction. It is thus possible by controlling the rate of circulation of acetylene to control the temperature level in the reaction vessel.

It is also an advantage that the process takes place in suspension, which is maintained by gas circulation; uniform temperature distribution is thereby readily achieved and maintained during the whole operation.

In a preferred method of operation the acetylene leaving the reactor is cooled in order to effect separation of water and propargyl alcohol and formaldehyde by condensation. The separated liquid may be either returned to the reactor or collected separately, or preferably returned at the early stage of operation and subsequently held separately for incorporation with the feed of a succeeding batch, as in this manner a purer reaction product is obtained.

While excellent results have been obtained when acetylene is used under a pressure of 20 atmospheres, it is not essential to operate at this particular pressure. The reaction has been successfully carried out using other pressures within the range 5 to 30 atm.

The invention is illustrated by the following examples:—

#### EXAMPLE 1

An aqueous solution of copper nitrate containing 2.03 kg. of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 5.46 l.

of deionised water was added to a solution of 764 g. of water glass ( $\text{Na}_2\text{O}$ , 17.1% and  $\text{SiO}_2$ , 36.3%) and of 277 g. of sodium hydroxide in 4.2 l. of deionised water with stirring, and maintained at a temperature of 40–50° C. for 90 minutes. The product was then filtered and resuspended in 8.4 l. of 0.3% aqueous caustic soda. The product was filtered again and resuspended in a similar quantity of water (8.4 l.). After filtration and drying at 100° C. *in vacuo* the product was roasted at 300° C. until no fumes appeared. The product was a black powder (945 g.) and contained 49.1% of copper.

825 g. of the black powder prepared as above were placed in an autoclave together with 8000 g. of an aqueous solution of formaldehyde (27% by weight). After venting with nitrogen, acetylene was admitted at 20 atm. at 90° C., and while the acetylide catalyst was being formed the temperature was raised to 100–105° C. Acetylene absorption ceased after 8 hours.

The product was filtered from the catalyst. It was found to contain 27.6% of butynediol and 6% of propargyl alcohol.

The same catalyst was reused, using 8150 g. of 37% solution of formaldehyde. During 4.5 hours 1420 g. of acetylene was absorbed. The product was filtered and contained 3940 g. of butynediol (39.2%), 430 g. of propargyl alcohol (4.3%) and 33 g. of formaldehyde (0.3%). The yield of butynediol on the formaldehyde was 92.2% and that of propargyl alcohol 7.6%.

The procedure was repeated nine times under similar conditions without deterioration of the catalyst.

#### EXAMPLE 2

To a stirred aqueous solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 241.5 g. in 680 ml. of water) was added a solution of water glass ( $\text{Na}_2\text{O}$  17.1% and  $\text{SiO}_2$  36.3%; 181 g.) and of caustic soda (22 g.) in water 500 g.). The product was washed with dilute aqueous caustic soda and repeatedly with water and was dried at 300° C. The product was a blue-grey powder containing 34.7% of copper.

This material was suspended in aqueous formaldehyde and treated with acetylene in the same way as described for the black powder in Example 1. The production of butynediol was very closely similar to that described in Example 1.

#### EXAMPLE 3

An aqueous solution of copper nitrate containing 2.03 kg. of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 5.46 l. of deionised water was added to a solution of 764 g. of water glass ( $\text{Na}_2\text{O}$  17.1% and  $\text{SiO}_2$  36.3%) and 277 g. of sodium hydroxide in 4.2 l. of deionised water with stirring and maintained at 40–50° C. for 90 minutes. The product was then filtered and re-suspended in 8.4 l. of 0.3% aqueous caustic soda. The

product was filtered again and re-suspended in a similar quantity of water. After filtration and drying at 100° C. the copper silicate (1145 g.) was roasted at 300° C. for 12 hours. The product (863 g.) was an almost black powder containing 50.2% of copper.

The reactor for the preparation of butynediol comprised a 20 litre stainless steel pressure vessel. This was fitted at the base with a gas inlet tube and gas distributor. It was also fitted close to the base with a tubular filter element of porous ceramic through which the reaction product was filtered. The gas leaving the reactor was passed through a water cooled condenser. The condensate separated into a catchpot in which it could either be held or from which it could be returned, to the reactor. The gas leaving the catchpot passed through a flash-back arrestor to a circulating compressor, operating in the range of 2–20 l./min. of compressed gas, which returned the gas to the reactor. Fresh acetylene compressed to the operational pressure was also available as required.

775 g. of copper silicate prepared as described above 7.95 kg. of a 37.2% aqueous solution of formaldehyde, and 150 g. of sodium bicarbonate were charged into the reactor, and treated with acetylene. The reaction was performed for 8 hours at 110–115° C. and at 18–20 atm. until 2.37 kg. of acetylene has been absorbed. The product was filtered during 25 minutes at 2 atm. The product was 6.4 kg. of an aqueous solution containing 37.8% of butynediol, 5.1% of propargyl alcohol and 0.7% of formaldehyde. Recycle condensate liquor was collected during the last two hours of the preparation, but it was added directly to the following preparation.

The copper acetylide prepared in the above preparation was reused in the above manner except that the reaction time was reduced to 5 hours in more than 20 preparations without deterioration of the catalyst. The propargyl alcohol contained in the reaction product was separated together with some water by fractional distillation and was added to the formaldehyde charge of subsequent preparations. Over the extended series of preparations a product containing a yield of 93% of butynediol, based on formaldehyde, and about 85% on acetylene was obtained as a 46% aqueous solution containing also 1% of propargyl alcohol and 0.5% of formaldehyde.

#### WHAT WE CLAIM IS:—

1. The modification of or improvement in the process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol described and claimed in Application No. 27318/54 (Serial No. 784,638) wherein a part of the solution of sodium silicate is replaced by a solution of sodium hydroxide,

potassium hydroxide or ammonium hydroxide.

2. A process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol comprising as a first stage the preparation of a basic copper silicate material containing 15—60% by weight of copper by mixing the requisite proportions of a copper salt, a solution of an alkali metal silicate and a solution of sodium hydroxide, potassium hydroxide, or ammonium hydroxide, and subsequently treating the thus formed basic copper silicate material with acetylene to convert the copper content of the material to copper acetylide.

3. A process according to Claim 1 or Claim 2 wherein the basic copper silicate material is separated, washed and dried prior to its treatment with acetylene.

4. Process according to Claim 3, wherein the basic copper silicate material is extruded into rods, pelleted, or converted into other suitable forms, prior to drying.

5. Process according to Claim 4, wherein the basic copper silicate material is mixed with material inert in respect to the reaction between acetylene and formaldehyde.

6. Process according to any of Claims 3 to 5, wherein the basic copper silicate material is impregnated with a further amount of copper prior to its treatment with acetylene.

7. Process according to any of Claims 1 to 6, wherein the conversion of the basic copper silicate material to the catalyst is effected by suspending the basic copper silicate material in aqueous formaldehyde and treating it with acetylene at a temperature above 60° C.

8. Process for the preparation of a catalyst

capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol substantially as hereinbefore described with reference to any of Examples 1 to 3.

9. A catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, when prepared by the process of any of Claims 1 to 8.

10. The method of preparing 2-butyne-1:4-diol by reaction between acetylene, and formaldehyde in the presence of a catalyst according to Claim 9.

11. Method according to Claim 10, wherein the catalyst is suspended in aqueous formaldehyde solution and maintained in suspension therein during the reaction period by passing through the solution acetylene under super-atmospheric pressure, the catalyst subsequently being separated from the liquid reaction product.

12. Method according to Claim 11, wherein the acetylene leaving the solution is cooled to effect separation of water, propargyl alcohol and formaldehyde therefrom by condensation.

13. Method according to Claim 12 wherein the liquid condensed by cooling the acetylene leaving the solution is returned to the solution.

14. Method according to Claim 12 wherein the liquid condensed by cooling the acetylene leaving the solution is returned to the solution during the initial stages of the reaction and is thereafter collected and added to the formaldehyde solution of a subsequent batch. 2-butyne-1:4-diol when prepared by the method of any of Claims 10 to 14.

P. L. SPENCER,  
Chartered Patent Agent.

#### PROVISIONAL SPECIFICATION

##### Catalysts

We, THE BRITISH OXYGEN COMPANY LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention to be described in the following statement:—

The present invention relates to catalysts and more particularly to copper acetylide catalysts for the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, and is an improvement in or modification of the invention described and claimed in our co-pending Application No. 27318/54.

2-butyne-1:4-diol (hereinafter referred to as butynediol) is usually prepared by reacting acetylene with an aqueous solution of formaldehyde in the presence of a catalyst consisting essentially of copper acetylide. The catalyst can be prepared by reacting an aqueous solution of a copper salt with acetylene under appropriate conditions, removing the precipitated copper acetylide and transferring it to the vessel in which the

acetylene and the formaldehyde are to be reacted. This procedure may give rise to difficulties in handling the free copper acetylide (which can decompose explosively when dry) and, moreover, it has been found that the catalyst particles are liable to attrition during the course of reaction, so that difficulties arise in separating the catalyst and the product liquor.

To obtain a more robust catalyst, it has been proposed to support the catalyst on a porous solid medium, the procedure being to deposit the copper salt on the support and to convert it to copper acetylide *in situ*. A preferred support has been silica gel, and in order to obtain a satisfactory catalyst, it has been necessary for the catalyst support to be specially prepared. Catalysts have been described in which the amount of copper held on the support was 10—12% by weight.

In Application No. 27318/54, there is claimed a process for the preparation of a

5 catalyst capable of catalysing the reaction  
between acetylene and formaldehyde to form  
2-butyne-1:4-diol comprising as a first stage,  
preparing a copper silicate material contain-  
15 ing 15—60% by weight of copper by mixing  
the requisite proportions of a solution of a  
copper salt and a solution of an alkali metal  
silicate, and subsequently converting the  
copper silicate material to the catalyst by  
10 treatment with acetylene.

It is an object of the present invention to  
provide a catalyst which is still more efficient  
than that described in Application No. 27318/  
54.

15 According to one aspect of the present  
invention, the process for the preparation of a  
catalyst capable of catalysing the reaction  
between acetylene and formaldehyde to form  
2-butyne-1:4-diol described and claimed in  
20 Application No. 27318/54 is modified by  
replacing a part of the solution of sodium  
silicate by a solution of sodium hydroxide,  
potassium hydroxide, and/or ammonium  
hydroxide.

25 According to another aspect of the present  
invention, a process for the preparation of a  
catalyst capable of catalysing the reaction  
between acetylene and formaldehyde to form  
2-butyne-1:4-diol, comprise as a first stage  
30 the preparation of a basic copper silicate  
material containing 15—60% by weight of  
copper by mixing the requisite proportions of  
a copper salt, a solution of alkali metal silicate,  
and a solution of sodium hydroxide, potassium  
35 hydroxide, and/or ammonium hydroxide, and  
subsequently converting the thus formed basic  
copper silicate material to the catalyst by  
treatment with acetylene.

40 The basic copper silicate precipitate may be  
separated, washed, and dried by heating in  
air to temperatures up to 500° C. or above,  
or by warming to only slightly elevated tem-  
perature under reduced pressure. When dry-  
45 ing at atmospheric pressure, the preferred  
upper temperature limit is 300° C. The dried  
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forms. It can, if desired be mixed with inert  
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It is possible, if desired, to impregnate the  
copper silicate material with further amounts  
of copper by immersion in a solution of a  
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way, the copper content of the final material  
can be raised to 60% or more, but this is not  
essential for the preparation of a useful  
catalyst.

65 It is possible to convert the precipitated

copper silicate into a copper acetylide catalyst  
without prior separation from its mother  
liquor but this is not a preferred method of  
operating the process of our invention.

70 It is sometimes considered desirable to  
incorporate in the catalyst for the reaction  
between acetylene and formaldehyde other  
materials generally described as "cuprene  
inhibitors". A particularly useful example of  
75 such inhibitors is bismuth.

The basic copper silicate catalyst prepared  
and used in accordance with the described in  
this patent application does not require the  
addition of cuprene inhibitors mentioned  
80 above as it has been found that cuprene forma-  
tion is almost negligible when the new method  
of preparation of the catalyst is used.

The copper silicate material may be con-  
verted into the actual catalyst used in the  
85 reaction by suspending it in water and treat-  
ing with acetylene, the wet material sub-  
sequently being transferred to the reactor in  
which the reaction between acetylene and  
formaldehyde is to be effected. Alternatively  
90 and preferably, the conversion may be carried  
out *in situ* in the reactor; in this case, the  
copper silicate material is added to the  
aqueous formaldehyde which is warmed above  
60° C. and acetylene is then fed to it. The  
95 catalyst so prepared is robust. In batch pro-  
cesses in which the catalyst is suspended in  
aqueous formaldehyde and the latter reacted  
with acetylene under pressure, the product  
liquor subsequently being separated from the  
catalyst which is then re-used, the catalysts  
100 of the present invention can be used repeatedly  
for a large number of successive operations.  
The separation of product liquor and catalyst  
remain facile even after much repeated use  
of the same bath of catalyst. In continuous opera-  
105 tion in which aqueous formaldehyde and  
acetylene are each flowed through a bed of  
catalyst, catalysts prepared according to the  
present invention are much less subject to  
attrition, to dislodgement of copper acetylide,  
110 or to blockages causing resistance to flow than  
are either unsupported copper acetylide or  
copper acetylide supported on prepared  
supports.

115 It is a further advantage of catalysts pre-  
pared in accordance with the present invention  
that a given amount of such a catalyst is  
capable of catalysing the reaction between  
acetylene and formaldehyde to a greater extent  
than the same amount of the catalyst which  
120 was the subject of Application No. 27318/54.

The invention is illustrated by the follow-  
ing examples:—

#### EXAMPLE 1

125 An aqueous solution of copper nitrate con-  
taining 2.30 kg.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 5.46 l.  
deionised water was added to a solution of  
764 g. of water glass ( $\text{Na}_2\text{O}$ , 17.1% and  $\text{SiO}_2$ ,  
36.3%) and of 277 g. of sodium hydroxide  
130 in 4.2 l. deionised water with stirring and

maintained at a temperature of 40—50° C. for 90 minutes. The product was then filtered and resuspended in dilute aqueous caustic soda 8.4 l. (0.3%). The product was filtered again and resuspended in a similar quantity of water (8.4 l.). After filtration and drying at 100° C. *in vacuo* the product was roasted at 300° C. until no fumes appeared. The product was a black powder 945 g. and contained 49.1% of copper.

825 g. of the black powder prepared as above was placed in an autoclave together with 8000 g. of a 27% (by weight) solution of formaldehyde. After venting with nitrogen, acetylene was admitted at 20 atm. at 90° C., and while the acetylide catalyst was being formed the temperature was raised to 100—105° C. Acetylene absorption ceased after 8 hours.

The product was filtered from the catalyst. It was found to contain 27.6% butynediol and 6% propargyl alcohol.

The same catalyst was reused, using 8150 g. of 37% solution of formaldehyde. During 4.5 hours 1420 g. of acetylene was absorbed. The product was filtered and contained 3940 g.

of butynediol (39.2%), 430 g. of propargyl alcohol (4.3%) and 33 g. of formaldehyde (0.3%). The yield of butynediol on the formaldehyde was 92.2% and that of propargyl alcohol 7.6%.

The procedure was repeated nine times under similar conditions without deterioration of the catalyst.

#### EXAMPLE 2

To a stirred aqueous solution of copper nitrite ( $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{H}_2\text{O}$ , 241.5 g. in 680 ml. of water) was added a solution of water glass ( $\text{Na}_2\text{O}$ , 17.1%;  $\text{SiO}_2$ , 36.3%, 181 g.) and of caustic soda (22 g.) in water (500 g.). The product was washed with dilute aqueous caustic soda and repeatedly with water and was dried at 300° C. The product was a blue-grey powder containing 34.7% of copper.

This material was suspended in aqueous formaldehyde and treated with acetylene in the same way as described for the black powder in Example 1. The production of butynediol was very closely similar to that described in Example 1.

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